

# Yb–Zn–Al ternary system: CaCu<sub>5</sub>-type derived compounds in the zinc-rich corner

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## Abstract

As part of a study of the Yb–Zn–Al system, this first article reports the synthesis and crystal structure of four compounds. The crystal structures were determined by single crystal diffractometer data for three of them: Yb<sub>3.36</sub>Zn<sub>30.94</sub>Al<sub>4.34</sub>, hexagonal, *P6/mmm*,  $a = 9.061(2) \text{ \AA}$ ,  $c = 8.878(2) \text{ \AA}$ ,  $Z = 1$ ,  $wR_2 = 0.055$ , with a structure derived from the SmZn<sub>11</sub> type; Yb<sub>6.4</sub>Zn<sub>46.8</sub>Al<sub>3.4</sub>, hexagonal, *P6/mmm*,  $a = 9.096(3) \text{ \AA}$ ,  $c = 13.178(5) \text{ \AA}$ ,  $Z = 1$ ,  $wR_2 = 0.060$ , with its own structure; Yb<sub>12.4</sub>Zn<sub>96.8</sub>Al<sub>4.4</sub>, hexagonal, *P6<sub>3</sub>/mmc*,  $a = 9.068(2) \text{ \AA}$ ,  $c = 26.369(8) \text{ \AA}$ ,  $Z = 1$ ,  $wR_2 = 0.088$ , with a structure derived from the U<sub>2</sub>Zn<sub>17</sub> type. The structure of Yb<sub>3</sub>Zn<sub>17.7</sub>Al<sub>4.3</sub>, tetragonal, *I4<sub>1</sub>/amd*,  $a = 8.920(1) \text{ \AA}$ ,  $c = 21.294(1) \text{ \AA}$ ,  $Z = 4$ , related to the Ce<sub>3</sub>Zn<sub>22</sub> type, was refined from powder data by the Rietveld method. The four structures belong to the same family, derived from the CaCu<sub>5</sub> type by replacing totally or partially some Ca atoms with dumbbells of partner elements. All the structures show no order for the aluminium atoms, but they preferentially occupy the dumbbells sharing the sites with zinc.

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## 1. Introduction

An investigation into the formation and crystal structure of the intermetallic phases existing in the Yb–Zn–Al system was undertaken more than 2 years ago, with the aim of finding compounds where ytterbium could show mixed or fluctuating valence behaviour. Most results obtained up to now, covering fourteen ternary phases, have been presented in a preliminary form [1]. Before starting the study no information regarding this system had been found in the literature; the existence of the YbZn<sub>1.65</sub>Al<sub>2.35</sub> phase with the tetragonal BaAl<sub>4</sub> structure type has been recently published [2]. In this first article, we report on the synthesis and crystal structure of four new intermetallics, Yb<sub>3.36</sub>Zn<sub>30.94</sub>Al<sub>4.34</sub> (8.7:80.1:11.2 at%), Yb<sub>6.4</sub>Zn<sub>46.8</sub>Al<sub>3.4</sub> (11.3:82.7:6.0 at%), Yb<sub>12.4</sub>Zn<sub>96.8</sub>Al<sub>4.4</sub> (10.9:85.2:3.9 at%) and Yb<sub>3</sub>Zn<sub>17.7</sub>Al<sub>4.3</sub> (12.0:70.8:17.2 at%), whose structures are all derived from the CaCu<sub>5</sub> type.

## 2. Experimental

The metals used were commercial products with high purity (99.9, 99.99 and 99.999 wt%, respectively, for ytterbium, zinc and aluminium). To avoid any weight losses due to possible volatilization of ytterbium and zinc during reaction and melting caused by the high vapour pressure of both metals, the alloys were prepared in sealed tantalum crucibles. Weighed amounts of the elements (small pieces for Yb and Zn, turnings for Al, prepared from surface-cleaned ingots; total mass of about 2 g) were directly pressed together into outgassed tantalum crucibles, which were sealed by arc welding under a flow of pure argon. Samples were melted by heating the crucibles in a high-frequency induction furnace up to 1100–1150 °C, well above their melting point, and shaken to ensure homogeneity. The crucibles were then sealed under vacuum in quartz tubes and annealed in resistance furnaces. Several samples were also examined by differential thermal analysis (DTA) to determine the liquidus and most of the characteristic temperatures. Specimens of about one-half

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of the alloy prepared as above and closed by arc welding into Mo crucibles were transferred to the DTA equipment and subjected to heating and cooling cycles at rates of 5 or 10 °C/min; accuracy in the temperature measurements was to within  $\pm 5$  °C. No contamination of the alloys due to reactivity towards the container material (Ta, Mo) was observed even when much higher temperatures than the liquidus were reached.

Light optical microscopy (LOM), scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) were used to investigate the microstructural appearance and the composition of the phases.

X-ray analysis was carried out by both powder and single crystal methods. Powder patterns were obtained by a Guinier–Stoe camera using the  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418$  Å) and pure Si as an internal standard ( $a = 5.4308$  Å); the Guinier patterns were indexed with the help of the LAZY-PULVERIX program [3] and the lattice parameters determined by least-squares methods. Single crystal intensities of  $\text{Yb}_{3.36}\text{Zn}_{30.94}\text{Al}_{4.34}$ ,  $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$  and  $\text{Yb}_{12.4}\text{Zn}_{96.8}\text{Al}_{4.4}$  were collected at 294 K on an MACH3 (Bruker-Nonius) diffractometer with graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.7107$  Å). Lattice parameters were obtained from 25 diffractometer-measured reflections at  $\theta = 24$ – $29^\circ$ . Owing to the irregular shape of the crystals, absorption correction was applied using  $\psi$ -scans of 2–4 top reflections. The SIR97 program [4] was used for the structure solution and the least-squares refinements based on  $F_o^2$  were made by SHELXL-97 [5], with anisotropic displacement parameters. Atomic coordinates were standardized with STRUCTURE TIDY [6] and structure drawings made with ATOMS [7]. Powder data of the  $\text{Yb}_3\text{Zn}_{17.7}\text{Al}_{4.3}$  compound were collected on a Philips PW1050/81 diffractometer with Bragg–Brentano geometry and Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418$  Å), in  $2\theta$  steps of  $0.02^\circ$  and a measuring time of 20 s/step. A total number

of 206 reflections and 4000 profile points were processed by the DBWS-9411 program [8], using pseudo-Voigt functions for the peak shape and a 5th-order polynomial for the background.

Crystal data of the three determined single-crystal structures are reported in Table 1. As can be seen, the number of the observed reflections with  $F_o > 4\sigma(F_o)$  in the three structures is very low compared with the independent reflections, reaching only 35% for the  $\text{Yb}_{12.4}\text{Zn}_{96.8}\text{Al}_{4.4}$  compound. This is a consequence of the particular structure, where the same sequence of layers is repeated many times along the  $c$ -axis.

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: (49)7247-808-666; E-mail: [crysdata@fiz.karlsruhe.de](mailto:crysdata@fiz.karlsruhe.de)) on quoting the depository number CSD-416334 (phase 1), CSD-416335 (phase 2), CSD-416336 (phase 3).

### 3. Results

#### 3.1. Thermal stability

The four compounds here reported are all likely to be formed by peritectic reaction. The reaction temperatures are very close to each other and not far from those of other Zn-rich phases found in this system (unpublished results). This fact along with undercooling effects (at least about 5 °C) make clear attribution of a thermal arrest to a given compound rather difficult and may even prevent it. However, it has been possible to detect more clearly the formation temperature of the compounds  $\text{Yb}_{12.4}\text{Zn}_{96.8}\text{Al}_{4.4}$  (hexagonal,  $\text{U}_2\text{Zn}_{17}$  type) and  $\text{Yb}_3\text{Zn}_{17.7}\text{Al}_{4.3}$  (tetragonal,  $\text{Ce}_3\text{Zn}_{22}$  type), the first forming nearly congruently at 750 °C, just below the liquidus at 755 °C, and the second at 720 °C. The other two  $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$  (hexagonal, its own

Table 1  
Crystal data of the compounds examined by single-crystal methods

	$\text{Yb}_{3.36}\text{Zn}_{30.94(5)}\text{Al}_{4.34(5)}$ (1)	$\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$ (2)	$\text{Yb}_{12.4}\text{Zn}_{96.8(1)}\text{Al}_{4.4(1)}$ (3)
Pearson code	<i>hP</i> 41-2.36	<i>hP</i> 63-6.4	<i>hP</i> 120-6.4
Space group	<i>P6/mmm</i> (No. 191)	<i>P6/mmm</i> (No. 191)	<i>P63/mmc</i> (No. 194)
<i>a</i> (Å)	9.061(2)	9.096(3)	9.068(2)
<i>c</i> (Å)	8.878(2)	13.178(5)	26.369(8)
Cell volume, formula weight	631.3(2), 2721.7	944.2(6), 4260.2	1877.8(8), 8595.7
Scan mode, $\theta$ range (deg)	$\omega$ - $\theta$ , 2-30	$\omega$ - $\theta$ , 2-30	$\omega$ , 2-30
Range in <i>hkl</i>	$\pm 11$ ; $0+11$ ; $\pm 12$ , $ h  >  k $	$0+11$ ; $0+11$ ; $\pm 18$ , and $-h-k-l$	$\pm 11$ ; $0+11$ ; $0+37$ , $ h  >  k $
Total number of reflections	2207	4308	3347
Absorption coefficient ( $\text{mm}^{-1}$ )	41.2	44.8	45.5
Transmission ratio (max/min)	3.90	1.61	3.18
Independent reflections, $R_{\text{int}}(F_o^2)$	417, 0.072	613, 0.086	1096, 0.094
Reflections with $F_o > 4\sigma(F_o)$	290	231	381
Number of parameters	32	44	65
Extinction coefficient	0.0027(1)	0.00073(4)	0.00053(2)
$wR(F_o^2)$ , all data	0.055	0.060	0.088
$R[F_o > 4\sigma(F_o)]$	0.025	0.026	0.031
Goodness of fit (S)	0.950	0.665	0.754
$\Delta\rho_{\text{min}}$ , $\Delta\rho_{\text{max}}$ ( $\text{e}/\text{\AA}^3$ )	-1.78, 1.83	-1.42, 2.33	-2.28, 2.67

structure type) and  $\text{Yb}_{3.36}\text{Zn}_{30.94}\text{Al}_{4.34}$  (hexagonal,  $\text{SmZn}_{11\sim}$  type) compounds showed the most probable formation temperature to be 735 and 715 °C, respectively.

### 3.2. The $\text{Yb}_{3.36}\text{Zn}_{30.94}\text{Al}_{4.34}$ phase (I)

Annealing an alloy with nominal “ $\text{Yb}_7\text{Zn}_{64}\text{Al}_{29}$ ” composition at 600 °C for 6 days resulted in the formation of two separate phases: one showing good crystallization, whereas the other was more compact and dropped to the bottom of the container. The former phase revealed single crystals of the  $\text{Yb}_{3.36}\text{Zn}_{30.94}\text{Al}_{4.34}$  phase (I). In order to check both symmetry and absorption correction reliability, three strong reflections with all 24 equivalents were collected and processed. The  $R_{\text{int}}(F_o^2)$  factor was 0.207 before and 0.036 after the absorption correction. So, the relatively high final  $R_{\text{int}}$  reported in Table 1 can be ascribed to the large number of unobserved reflections. The same holds for the other two determined single crystal structures.

Preliminary data showed this structure to be very similar to the  $\text{SmZn}_{11\sim}$  type [9], described in the  $P6/mmm$  space group and this model was taken as the starting point in the refinement. Three Zn positions, called X1, X2 and X3, were found to be filled with a Zn/Al mixture, and similarly to the parent structure, the Yb2 atom (1/3, 2/3, 0) is an alternative to the pair of X2 atoms. On the other hand, the possible Yb atom (0, 0, 1/2), partially occupying the parent model, is now absent leaving the X3 position fully occupied. The sum of the occupation factors of the alternative Yb2 and X2 atoms was fixed to 1, and the occupancy varied step by step, until reasonable displacement parameters and Fourier difference values were obtained. Instead, the mixed occupation of the three Zn/Al atoms was refined. In the last cycles, all the occupancies were fixed to the pre-determined values.

Atomic coordinates and equivalent isotropic displacement parameters are reported in Table 2, while interatomic distances are given in Table 3 up to values not exceeding 13% of the sum of the metallic radii for CN12 [10]. The same also apply to Tables 5 and 7. The lattice parameters

Table 2

Atomic coordinates and equivalent isotropic displacement parameters of  $\text{Yb}_{3.36}\text{Zn}_{30.94(5)}\text{Al}_{4.34(5)}$  (I)

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$ (Å <sup>2</sup> )
Yb1	2 <i>d</i>	1/3	2/3	1/2	0.0091(2)
Yb2 <sup>a</sup>	2 <i>c</i>	1/3	2/3	0	0.012(1)
Yb3	1 <i>a</i>	0	0	0	0.0076(3)
Zn1	12 <i>o</i>	0.1674(1)	2 <i>x</i>	0.2418(1)	0.0132(2)
Zn2	6 <i>k</i>	0.2971(2)	0	1/2	0.0138(3)
Zn3	6 <i>i</i>	1/2	0	0.2754(2)	0.0152(3)
X1 <sup>b</sup>	6 <i>j</i>	0.3527(2)	0	0	0.0283(5)
X2 <sup>b</sup>	4 <i>h</i>	1/3	2/3	0.1460(5)	0.0117(9)
X3 <sup>b</sup>	2 <i>e</i>	0	0	0.3522(3)	0.0136(6)

<sup>a</sup>Occ. = 0.18.

<sup>b</sup>X1 = 0.797(8) Zn + 0.203 Al; X2 = 0.17(1) Zn + 0.65 Al; X3 = 0.74(1) Zn + 0.26 Al.

Table 3

Interatomic distances (Å) in  $\text{Yb}_{3.36}\text{Zn}_{30.94(5)}\text{Al}_{4.34(5)}$  (I)

Yb1-	2 X2	3.143(4)	Yb2-	6 X1	2.936(1)
	6 Zn2	3.197(1)		6 Zn1	3.375(1)
	6 Zn3	3.289(1)		6 Zn3	3.581(1)
	6 Zn1	3.469(1)	Zn1-	2 Zn3	2.627(1)
Yb3-	2 X3	3.127(3)		2 Zn1	2.627(1)
	6 X1	3.196(2)		2 Zn2	2.674(1)
	12 Zn1	3.393(1)		2 X1	2.680(1)
				X2 <sup>a</sup>	2.740(2)
Zn2-	4 Zn1	2.674(1)		X3	2.804(2)
	2 Zn2	2.692(2)		Yb2 <sup>a</sup>	3.375(1)
	2 Zn3	2.712(2)		Yb3	3.393(1)
	2 X3	2.995(2)		Yb1	3.469(1)
	2 Yb1	3.197(1)	Zn3-	4 Zn1	2.627(1)
X1-	X1	2.669(4)		2 Zn2	2.712(2)
	4 Zn1	2.680(1)		2 X1	2.786(2)
	2 Zn3	2.786(2)		2 X2 <sup>a</sup>	2.857(2)
	2 Yb2	2.936(1)		2 Yb1	3.289(1)
	Yb3	3.196(2)		2 Yb2 <sup>a</sup>	3.581(1)
X2-	X2	2.592(8)	X3-	X3	2.624(6)
	3 Zn1	2.740(2)		6 Zn1	2.804(2)
	3 Zn3	2.857(2)		6 Zn2	2.995(2)
	Yb1	3.143(4)		Yb3	3.127(3)

<sup>a</sup>Alternative atoms.

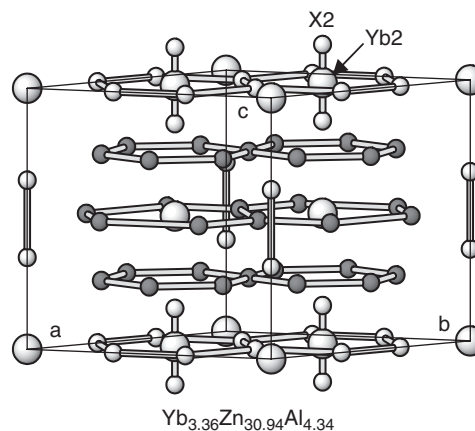


Fig. 1. Atomic arrangement in  $\text{Yb}_{3.36}\text{Zn}_{30.94}\text{Al}_{4.34}$  (I) with a structure derived from the  $\text{SmZn}_{11\sim}$  type. Open large circles: Yb; open small circles: Zn/Al; full circles: Zn. The picture is somewhat idealized and the atoms connected in the hexagons are not always at bond distance.

obtained from a Guinier powder pattern were  $a = 9.068(1)$  Å,  $c = 8.889(1)$  Å, in agreement with the single crystal values. The atomic arrangement in (I) is shown in Fig. 1. As for the parent  $\text{CaCu}_5$  type, the structure is built up by two kinds of layers alternating along the *c* axis. One of them is a  $6^3$  layer formed by the partner elements (Zn or Zn/Al) and containing the Yb atoms centering the hexagons; the other is a kagomé layer formed by Zn atoms. The basal plane shows the alternative Yb2 and

X2–X2 pair, while the X3–X3 dumbbell completely replaces the corresponding Yb atom at  $c/2$ .

Other ternary disordered compounds crystallizing with the  $\text{SmZn}_{11\sim}$  type were found in the Nd–Cu–Ga and Sm–Cu–Ga systems [11,12].

### 3.3. The $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$ phase (2)

Single crystals of the  $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$  phase (2) were found in a sample of “ $\text{Yb}_{12}\text{Zn}_{72}\text{Al}_{16}$ ” composition annealed at  $750^\circ\text{C}$  for 5 days. The structure was solved in the  $P6mm$  space group, but, shifting the origin, was described and refined in the centrosymmetric  $P6/mmm$  space group. The starting model contained three Yb and seven Zn sites. It was at once evident that a Yb site was defective, and in alternate cycles its occupancy or anisotropic displacement parameters were allowed to vary. After some cycles of anisotropic refinement, the Fourier difference synthesis revealed two other peaks corresponding to a pair of atoms which are alternatives to the defective Yb. These atoms, labelled X1 and X2, were assigned a mixture of Zn and Al atoms, and the same was applied to the X3 site initially filled with Zn. In the last cycles the occupation factors of Yb1, X1 and X2 atoms were fixed to the previously obtained values.

At this point the collected data were again processed applying the trigonal  $\bar{3}1m$  and  $\bar{3}m1$  Laue symmetry. Only the first one showed a somewhat significant improvement, lowering  $R_{\text{int}}(F_o^2)$  to 0.069, compared with 0.086 for the  $6/mmm$  symmetry, and the refinement was then repeated in the  $P\bar{3}1m$  space group. Despite the larger number of refined parameters (59 instead of 44), no improvement was observed: the displacement parameters of two atoms resulted “nonpositive definite”, while agreement factors and Fourier difference results were clearly worse.

Atomic coordinates and equivalent isotropic displacement parameters of the structure refined in the  $P6/mmm$  space group are reported in Table 4, while interatomic distances are given in Table 5. EPMA results gave the  $\text{Yb}_{11.5}\text{Zn}_{83.5}\text{Al}_5$  composition, in good agreement with the crystal refinement. The lattice parameters determined from a Guinier powder pattern were  $a = 9.096(1)\text{Å}$ ,  $c = 13.175(1)\text{Å}$ , in very good agreement with the single crystal values. Since no similar structure has been found in the literature, it may be considered a new structure. The picture of (2) in Fig. 2 shows a very similar situation to that of phase (1). The Yb1 atom is alternative to the couple X1–X2, while the X3–X3 dumbbell completely replaces the corresponding Yb atom in the basal plane. The coordination polyhedra around the three Yb atoms are hexagonal prisms capped on all faces, reaching CN20 as in the parent  $\text{CaCu}_5$  type. Distorted icosahedra are found for the Zn1, Zn3, Zn4, Zn5 and Zn6 atoms, while the polyhedron of Zn2 with a lower CN10 can be described as a Zn trigonal prism with four equatorial atoms, three emerging from the lateral faces and the fourth from an edge. With regard to the atoms with mixed Zn/Al occupation, X1 and X2 are

Table 4

Atomic coordinates and equivalent isotropic displacement parameters of  $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$  (2)

Atom	Position	x	y	z	$U_{\text{eq}}$ ( $\text{Å}^2$ )
Yb1 <sup>a</sup>	4h	1/3	2/3	0.3314(6)	0.0082(4)
Yb2	2e	0	0	0.3373(4)	0.0073(11)
Yb3	2c	1/3	2/3	0	0.0069(11)
Zn1	12o	0.1686(4)	2x	0.1727(4)	0.012(1)
Zn2	12n	0.3493(4)	0	0.3337(4)	0.038(1)
Zn3	6m	0.1624(4)	2x	1/2	0.027(2)
Zn4	6j	0.3024(6)	0	0	0.013(1)
Zn5	6i	1/2	0	0.1555(4)	0.014(1)
Zn6	3g	1/2	0	1/2	0.012(2)
X1 <sup>b</sup>	4h	1/3	2/3	0.235(1)	0.011(2)
X2 <sup>b</sup>	4h	1/3	2/3	0.432(1)	0.011(2)
X3 <sup>b</sup>	2e	0	0	0.1012(9)	0.010(3)

<sup>a</sup>occ. = 0.6.

<sup>b</sup>X1 = X2 = 0.2 Zn + 0.2 Al, isotropically refined; X3 = 0.11(2) Zn + 0.89 Al.

surrounded by a hexagonal bipyramid, and X3 by a bicapped hexagonal antiprism. The Yb1–X2 distance becomes possible if the two atoms lie in different semicells.

### 3.4. The $\text{Yb}_{12.4}\text{Zn}_{96.8}\text{Al}_{4.4}$ phase (3)

Crystals from an alloy of “ $\text{Yb}_{12.5}\text{Zn}_{72.5}\text{Al}_{15}$ ” composition annealed at  $700^\circ\text{C}$  for 35 days were isolated with hexagonal symmetry and possible  $P6_3mc$ ,  $P\bar{6}2c$  and  $P6_3/mmc$  space groups. A search in the TYPIC collection [13] showed symmetry and lattice parameters compatible with the ordered  $\text{U}_2\text{Zn}_{17}$  type with  $P6_3/mmc$  space group. This model was taken as the starting point in the refinement with a full occupancy of the zinc sites. Of the ten Zn atoms, three (later called X1, X2 and X3) showed twice or three times the isotropic displacement parameters than the average of the other positions, indicating a probable mixed Zn/Al occupation. During the refinement, two other peaks which were alternatives to the X1–X2 and X3–X3 pairs appeared in the Fourier difference synthesis. Likewise the (1) and (2) structures, these sites were partially filled with Yb atoms and the sum of the occupancy of the alternative atoms was constrained to 1. Occupation factors were varied step by step, until reasonable displacement parameters and Fourier residuals were obtained. In the last cycles all the occupation factors and the isotropic displacement parameters of the defective Yb atoms were fixed to their pre-determined values.

Atomic coordinates and equivalent isotropic displacement parameters of this compound (3), are reported in Table 6, while interatomic distances are given in Table 7. EPMA results gave the  $\text{Yb}_{11.5}\text{Zn}_{84}\text{Al}_{4.5}$  composition, in good agreement with the crystal refinement. The lattice parameters obtained from a Guinier powder pattern were  $a = 9.066(1)\text{Å}$ ,  $c = 26.368(6)\text{Å}$ , in very good agreement with the single crystal values. The atomic arrangement in (3) is drawn in Fig. 3. Unlike structures (1) and (2), here the

Table 5  
Interatomic distances (Å) in  $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$  (2)

Yb1-	6 Zn2	2.962(2)	Yb2-	X3	3.11(1)
	X2	3.12(2)		6 Zn2	3.177(4)
	3 Zn1	3.333(7)		6 Zn3	3.338(6)
	3 Zn6	3.439(5)		6 Zn1	3.430(6)
	3 Zn3	3.491(7)		Yb2	4.287(9)
	3 Zn5	3.503(6)	Zn1-	2 Zn5	2.621(7)
	Yb3	4.367(7)		2 Zn2	2.652(6)
Yb3-	2 X1 <sup>a</sup>	3.09(1)		2 Zn1	2.656(6)
	6 Zn4	3.182(3)		2 Zn4	2.673(4)
	6 Zn5	3.331(4)		X1 <sup>a</sup>	2.721(7)
	6 Zn1	3.451(5)		X3	2.819(7)
	2 Yb1 <sup>a</sup>	4.367(7)		Yb1 <sup>a</sup>	3.333(7)
Zn2-	Zn6	2.585(5)		Yb2	3.430(6)
	2 Zn1	2.652(6)		Yb3	3.451(5)
	2 Zn3	2.713(4)	Zn3-	2 Zn3	2.559(7)
	Zn5	2.719(7)		2 Zn6	2.660(9)
	Zn2	2.742(7)		4 Zn2	2.713(4)
	2 Yb1	2.962(2)		2 X2 <sup>a</sup>	2.840(8)
	Yb2	3.177(4)		2 Yb2	3.338(6)
				2 Yb1 <sup>a</sup>	3.491(7)
Zn4-	4 Zn1	2.673(4)	Zn5-	4 Zn1	2.621(7)
	2 Zn5	2.726(5)		2 Zn2	2.719(7)
	2 Zn4	2.751(5)		2 Zn4	2.726(5)
	2 X3	3.057(7)		2 X1 <sup>a</sup>	2.826(6)
	2 Yb3	3.182(3)		2 Yb3	3.331(4)
Zn6-	4 Zn2	2.585(5)		2 Yb1 <sup>a</sup>	3.503(6)
	4 Zn3	2.660(9)	X1-	X2	2.59(2)
	4 X2 <sup>a</sup>	2.776(5)		3 Zn1	2.721(7)
	4 Yb1 <sup>a</sup>	3.439(5)		3 Zn5	2.826(6)
X2-	X1	2.59(2)		Yb3	3.09(1)
	3 Zn6	2.776(5)	X3-	X3	2.67(2)
	3 Zn3	2.840(8)		6 Zn1	2.819(7)
	Yb1	3.12(2)		6 Zn4	3.057(7)
				Yb2	3.11(1)

<sup>a</sup>Alternative atoms.

couples X1–X2 and X3–X3 always partially replace the corresponding Yb1 and Yb6 atoms.

### 3.5. The $\text{Yb}_3\text{Zn}_{17.7}\text{Al}_{4.3}$ phase (4)

A low quality single crystal was eventually found in an alloy with “ $\text{Yb}_{12.5}\text{Zn}_{72.5}\text{Al}_{15}$ ” composition annealed at 660 °C for 10 days. However, it was sufficient to give a body-centered tetragonal cell metrically similar to that of the  $\text{Ce}_3\text{Zn}_{22}$  type [14]. Other trials were repeated on another sample with composition  $\text{Yb}_{12}\text{Zn}_{68}\text{Al}_{20}$  annealed at 660 °C for 29 days, but the microcrystalline nature of the alloy together with its homogeneity suggested that the Rietveld method should be applied. The refinement started using the coordinates of the isotypic  $\text{Pu}_3\text{Zn}_{22}$  [15] and the

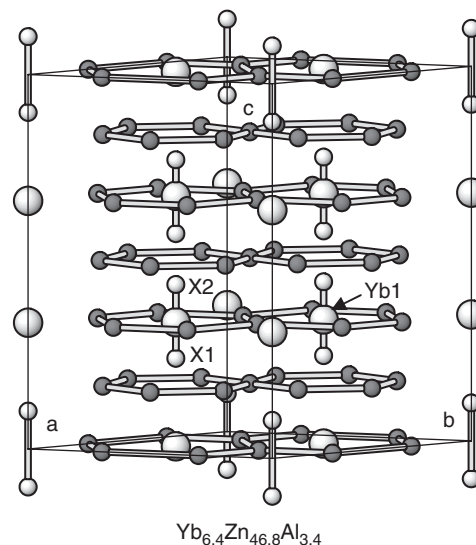


Fig. 2. Atomic arrangement in  $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$  (2). Atom labels and idealization as given in Fig. 1.

Table 6  
Atomic coordinates and equivalent isotropic displacement parameters of  $\text{Yb}_{12.4}\text{Zn}_{96.8(1)}\text{Al}_{4.4(1)}$  (3)

Atom	Position	x	y	z	$U_{\text{eq}}$ (Å <sup>2</sup> )
Yb1 <sup>a</sup>	4f	1/3	2/3	0.0774(10)	0.0084
Yb2	4f	1/3	2/3	0.5847(1)	0.0083(3)
Yb3	4e	0	0	0.0812(1)	0.007(1)
Yb4	2d	1/3	2/3	3/4	0.010(1)
Yb5	2c	1/3	2/3	1/4	0.008(1)
Yb6 <sup>a</sup>	2b	0	0	1/4	0.0084
Zn1	24l	0.0326(3)	0.3661(4)	0.0832(2)	0.0136(6)
Zn2	12k	0.1613(5)	2x	0.5064(1)	0.014(1)
Zn3	12k	0.1664(7)	2x	0.1668(2)	0.008(1)
Zn4	12k	0.1686(6)	2x	0.6603(2)	0.012(1)
Zn5	12k	0.5046(5)	2x	0.1730(2)	0.013(1)
Zn6	12j	0.3029(6)	0.0037(3)	1/4	0.014(1)
Zn7	6g	1/2	0	0	0.015(2)
X1 <sup>b</sup>	4f	1/3	2/3	0.0331(3)	0.014(1)
X2 <sup>b</sup>	4f	1/3	2/3	0.1330(3)	0.016(1)
X3 <sup>b</sup>	4e	0	0	0.2001(3)	0.010(2)

<sup>a</sup>Yb1: occ. = 0.08; Yb6: occ. = 0.04; both isotropically refined.

<sup>b</sup>X1 = 0.61(3) Zn + 0.31 Al; X2 = 0.63(3) Zn + 0.29 Al; X3 = 0.47(3) Zn + 0.49 Al.

lattice parameters determined by Guinier photograph,  $a = 8.920(1)$  Å,  $c = 21.294(2)$  Å. The results are reported in Table 8, while the observed and calculated X-ray pattern is shown in Fig. 4. With the exception of Zn in 8c, all the Zn positions have a mixed Zn/Al occupation resulting in the final formula  $\text{Yb}_3\text{Zn}_{17.70(5)}\text{Al}_{4.30(5)}$ . EPMA results gave the  $\text{Yb}_{12}\text{Zn}_{72.5}\text{Al}_{15.5}$  composition, in good agreement with the Rietveld refinement. The refined atomic coordinates of the phase (4) are very close to the values of the starting model and the shortest interatomic distances are X1–X2 2.58(1) Å and Yb1–X4 3.09(1) Å.

Table 7  
Interatomic distances (Å) in  $\text{Yb}_{12.4}\text{Zn}_{96.8(1)}\text{Al}_{4.4(1)}$  (**3**)

Yb1-	6 Zn1	2.730(3)	Yb2-	X1 <sup>a</sup>	3.105(7)
	3 Zn7	3.32(2)		6 Zn1	3.181(3)
	3 Zn2	3.49(2)		3 Zn4	3.267(8)
	3 Zn3	3.53(2)		3 Zn2	3.400(7)
	3 Zn5	3.69(2)		3 Zn7	3.441(2)
	Yb2	4.27(3)		3 Zn5	3.449(7)
				Yb1 <sup>a</sup>	4.27(3)
Yb3-	X3	3.135(7)	Yb4-	Yb4	4.359(3)
	6 Zn1	3.183(3)		6 Zn6	3.155(4)
	3 Zn2	3.211(7)		6 Zn5	3.256(7)
	3 Zn4	3.371(8)		6 Zn4	3.506(8)
	3 Zn2	3.428(6)		2 Yb2	4.359(3)
	3 Zn3	3.453(9)	Yb5-	2 X2	3.086(7)
	Yb3	4.281(6)		6 Zn6	3.204(4)
Yb6-	6 Zn6	2.730(5)		6 Zn5	3.371(7)
	6 Zn3	3.413(9)		6 Zn3	3.419(9)
	6 Zn4	3.550(8)	Zn2-	2 Zn2	2.556(8)
Zn1-	Zn7	2.596(4)		2 Zn7	2.666(9)
	Zn3	2.604(5)		2 Zn1	2.717(4)
	Zn2	2.717(4)		2 Zn1	2.750(5)
	Zn4	2.721(5)		X1 <sup>a</sup>	2.895(8)
	Zn1	2.724(7)		Yb3	3.211(7)
	Zn1	2.728(5)		Yb2	3.400(7)
	Yb1 <sup>a</sup>	2.730(3)		Yb3	3.428(6)
	Zn5	2.750(6)		Yb1 <sup>a</sup>	3.49(2)
	Zn2	2.750(5)	Zn3-	2 Zn1	2.604(5)
	X2 <sup>i</sup>	3.025(4)		2 Zn6	2.611(4)
	X1 <sup>j</sup> <sup>a</sup>	3.030(4)		2 Zn4	2.636(15)
	Yb2	3.181(3)		2 Zn5	2.662(14)
	Yb3	3.183(3)		X3 <sup>b</sup>	2.757(10)
Zn4-	2 Zn5	2.588(12)		X2 <sup>a</sup>	2.769(10)
	2 Zn3	2.636(15)		Yb6 <sup>b</sup>	3.413(9)
	2 Zn1	2.721(5)		Yb5	3.419(9)
	2 Zn6	2.731(4)		Yb3	3.453(9)
	X3 <sup>a</sup>	2.848(9)		Yb1 <sup>a</sup>	3.53(2)
	Yb2	3.267(8)	Zn5-	2 Zn4	2.588(12)
	Yb3	3.371(8)		2 Zn3	2.662(14)
	Yb4	3.506(8)		2 Zn6	2.717(5)
	Yb6 <sup>a</sup>	3.550(8)		2 Zn1	2.750(6)
Zn6-	2 Zn3	2.611(4)		X2 <sup>a</sup>	2.890(8)
	Zn6	2.679(7)		Yb4	3.256(7)
	2 Zn5	2.717(5)		Yb5	3.371(7)
	Yb6 <sup>a</sup>	2.730(5)		Yb2	3.449(7)
	2 Zn4	2.731(4)		Yb1 <sup>a</sup>	3.69(2)
	Zn6	2.780(7)	Zn7-	4 Zn1	2.596(4)
	2 X3 <sup>a</sup>	3.030(6)		4 Zn2	2.666(9)
	Yb4	3.155(4)		2 X1 <sup>a</sup>	2.759(2)
	Yb5	3.204(4)		2 Yb1 <sup>a</sup>	3.32(2)
X1-	X2	2.634(8)		2 Yb2	3.441(2)
	3 Zn7	2.759(2)	X3-	X3	2.633(13)
	3 Zn2	2.895(8)		3 Zn3	2.757(10)
	6 Zn1	3.030(4)		3 Zn4	2.848(9)
	Yb2	3.105(7)		6 Zn6	3.030(6)
X2-	X1	2.634(8)		Yb3	3.135(7)
	3 Zn3	2.769(10)			
	3 Zn5	2.890(8)			
	6 Zn1	3.025(4)			
	Yb5	3.086(7)			

<sup>a,b</sup>Alternative atoms.

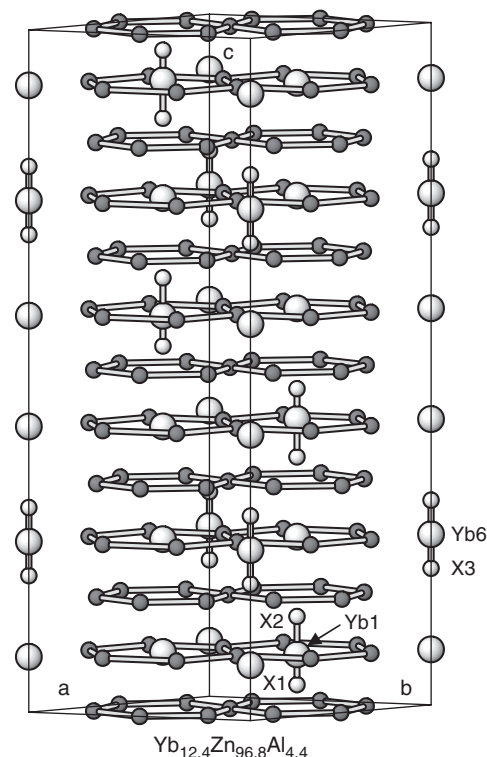


Fig. 3. Atomic arrangement in  $\text{Yb}_{12.4}\text{Zn}_{96.8}\text{Al}_{4.4}$  (**3**) with a structure derived from the  $\text{U}_2\text{Zn}_{17}$  type. Atom labels and idealization as given in Fig. 1.

Table 8  
Atomic coordinates and isotropic displacement parameters for  $\text{Yb}_3\text{Zn}_{17.70(5)}\text{Al}_{4.30(5)}$  (**4**)

Atom	Position	x	y	z	B (Å <sup>2</sup> )
Yb1	8e	0	1/4	0.2547(1)	2.7(1)
Yb2	4a	0	3/4	1/8	2.2(1)
X1 <sup>a</sup>	32i	0.2315(3)	0.0080(5)	0.1894(2)	3.13(7)
X2 <sup>a</sup>	16h	0	0.0288(6)	0.3757(4)	3.08(6)
X3 <sup>a</sup>	16h	0	0.1017(5)	0.1172(3)	2.3(2)
X4 <sup>a</sup>	16h	0	0.5959(5)	0.2611(3)	2.5(2)
Zn	8c	0	0	0	2.9(2)

Space group  $I4_1/amd$  (No.141), origin at centre,  $R_{wp} = 0.035$ ,  $R_B = 0.093$ .  
<sup>a</sup>X1 = 0.850(6) Zn + 0.150 Al; X2 = 0.596(2) Zn + 0.404 Al; X3 = 0.77(1) Zn + 0.23 Al; X4 = 0.86(1) Zn + 0.14 Al.

### 3.6. General considerations

The disorder in structures (**1**), (**2**) and (**3**), due to the alternative presence of a Yb atom and a Zn/Al dumbbell, gives rise to two closely related effects originating from the same average situation and involving the Zn (or Zn/Al) atom coplanar with that Yb atom. One is the value of its anisotropic displacement parameters and the other is its distance from the defective ytterbium. We refer to the atoms X1 for (**1**), Zn2 for (**2**), Zn1 and Zn6 for (**3**). In structures (**1**) and (**2**), both with  $P6/mmm$  space group,  $U_{22} = 0.064(1)\text{Å}^2$  for X1 (**1**) and  $U_{22} = 0.099(3)\text{Å}^2$  for

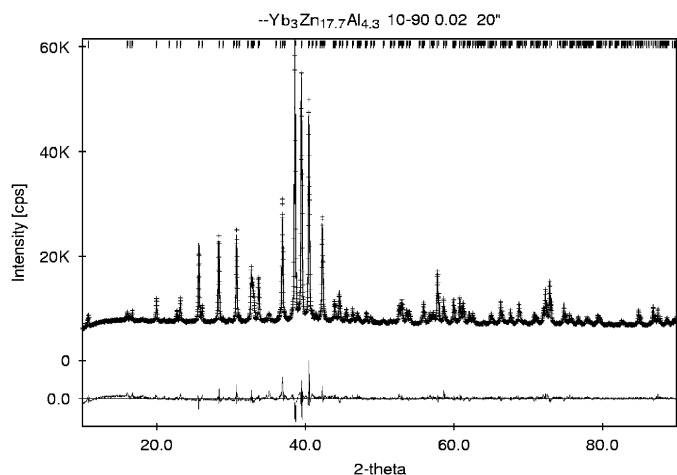


Fig. 4. Observed X-ray powder pattern (crosses) and Rietveld refinement profile (solid line) for the  $\text{Yb}_3\text{Zn}_{17.7}\text{Al}_{4.3}$  phase (4). The lower profile gives the difference between observed and calculated data; the Bragg angle positions are indicated by vertical bars.

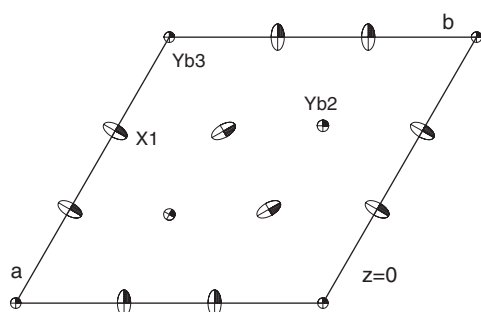


Fig. 5. Thermal ellipsoids of the atoms at  $z = 0$  in the  $\text{Yb}_{3.36}\text{Zn}_{30.94}\text{Al}_{4.34}$  structure (1). The Yb2 atom, alternative to the X2–X2 dumbbell, has a 18% occupancy.

Zn2 (2) are observed, compared to the occurrence of ytterbium with 18% and 60% occupancy, respectively. As a result, a thermal ellipsoid points towards both defective Yb atoms lying in the same plane, as shown in Fig. 5 for structure (1). These findings agree with the previous observations for the parent  $\text{SmZn}_{11\sim}$  [9] and  $\text{UZn}_{12\sim}$  [16] structures, from which the structure (1) can be derived with very small changes: the Zn atom coplanar with Sm (15% occupancy) or with U (24% occupancy) has a  $U_{22}$  value of 0.061 and 0.086  $\text{\AA}^2$ , respectively. On the other hand, an attempt to introduce split positions for the X1 atom in (1) and Zn2 atom in (2), improved the displacement parameters, but made distances between the involved atoms and some Yb atoms too short.

For structure (3) with  $P6_3/mmc$  space group, the thermal ellipsoids of Zn1 and Zn6 are normal and the respective defective Yb sites are occupied by 8% and 4%. Then, the elongation of the thermal ellipsoid in the defective Yb direction is approximately proportional to the degree of occupation of the Yb site.

Regarding the distance of the Zn (or Zn/Al) atom from the defective Yb, the lower the Yb occupancy the shorter

the distance becomes. What may actually be observed is an average distance as a result of ordered situations: presence of Yb only in a certain percentage of cells and presence of a dumbbell in the others. If the Yb occupancy is very low as in structure (3), with 8% and 4%, very contracted Zn1–Yb1 and Zn6–Yb6 distances of 2.730  $\text{\AA}$  are found, because the configuration with the X1–X2 or X3–X3 pairs prevails and Zn1 and Zn6 approach these pairs. Where the Yb2 occupancy increases to 18%, as in structure (1), the X1–Yb2 distance increases to 2.936  $\text{\AA}$  and eventually in structure (2), with a 60% occupancy of Yb1, the Zn2–Yb1 distance becomes 2.962  $\text{\AA}$ . Therefore, in these last two structures the atom pairs are no longer included in the coordination of the X1 or Zn2 atoms.

As noted by the authors, in  $\text{SmZn}_{11\sim}$  [9], where the Sm(4) site is only occupied by 4%, the Zn(3)–Sm(4) distance of 2.642  $\text{\AA}$  “shows an unrealistically exaggerated contraction” since it is an average distance. This effect is also apparent to a much lesser degree in the Zn(2)–Sm(3) distance with a 15% occupancy of Sm(3).

Voids in the structures of (1), (2) and (3) were sought using the CAVITY program [17] by choosing the prevalent atomic arrangement between the alternatives. The largest holes are always tetrahedrally delimited by 4 Zn, with a radius less than 0.45  $\text{\AA}$ , and located at (1/2,0,1/2), (1/2,0,0) and (0.36,0.18,0.08), respectively.

#### 4. Discussion

The structures adopted by the four examined phases of the Yb–Zn–Al system are found in neither the Yb–Zn nor the Yb–Al system, even though three of them occur in other rare earth–zinc or uranium–zinc compounds. The introduction of aluminium seems to stabilize these structures, which are otherwise unstable in the corresponding binary systems.

The four structures belong to the family derived from the  $\text{CaCu}_5$  type by replacing part of the Ca atoms with dumbbells of partner elements. This mechanism produces a large number of new binary and ternary compounds with cells which are multiple of the basic parent type. The substitution on the Ca sites may be total or only partial, giving rise to ordered or partially disordered structures. Examples of ordered structures are  $\text{ThMn}_{12}$ ,  $\text{Th}_2\text{Zn}_{17}$ ,  $\text{Th}_2\text{Ni}_{17}$ ,  $\text{Ce}_3\text{Zn}_{22}$ . In several cases, both the disordered and ordered versions exist, as, for instance, the already cited  $\text{SmZn}_{11\sim}$  (*hP*42–3.34) [9] and the ordered  $\text{EuAg}_4\text{In}_8$  (*hP*39) [18]. Other examples of disordered structures can be found in the phases of the Yb–Fe–Al system close to the Yb:(Fe, Al) = 2:17 composition [19].

The members of this family are described in TYPIX [13] as an intergrowth of the  $\text{CaCu}_5$  and  $\text{Zr}_4\text{Al}_3$  types, the last being the counterpart of the  $\text{CaCu}_5$  type with substitution of a Zr–Zr pair for calcium. The general formula of these phases is  $R_{1-x}(M, M')_{5+2x}$ , where  $x$  is the ratio of the number of  $\text{Zr}_4\text{Al}_3$ -type blocks to the total number of  $\text{CaCu}_5$ - and  $\text{Zr}_4\text{Al}_3$ -type blocks. According to the example

given in TYPIX, the chemical formula can be decomposed into the two intergrown segments taken from the  $\text{CaCu}_5$  and  $\text{Zr}_4\text{Al}_3$  types, respectively. These formulae for the four examined compounds are listed below, together with the relations of cell parameters and volume to those ( $a'$ ,  $c'$ ,  $V'$ ) of the parent  $\text{CaCu}_5$  structure:

- (1)  $0.56[\text{YbT}_2^{[6p]} \text{Zn}_3] + 0.44[(\text{Zn}/\text{Al}-\text{Zn}/\text{Al})\text{T}_2^{[6p]} \text{Zn}_3]$   
 $a = a'\sqrt{3}$ ,  $c = 2c'$ ,  $V = 6V'$ ,
- (2)  $0.71[\text{YbZn}_2^{[6p]} \text{Zn}_3] + 0.29[(\text{Zn}/\text{Al}-\text{Zn}/\text{Al})\text{Zn}_2^{[6p]} \text{Zn}_3]$   
 $a = a'\sqrt{3}$ ,  $c = 3c'$ ,  $V = 9V'$ ,
- (3)  $0.69[\text{YbZn}_2^{[6p]} \text{Zn}_3] + 0.31[(\text{Zn}/\text{Al}-\text{Zn}/\text{Al})\text{Zn}_2^{[6p]} \text{Zn}_3]$   
 $a = a'\sqrt{3}$ ,  $c = 6c'$ ,  $V = 18V'$ ,
- (4)  $3/4[\text{YbT}_2^{[6p]} \text{T}_3] + 1/4[(\text{Zn}/\text{Al}-\text{Zn}/\text{Al})\text{T}_2^{[6p]} \text{T}_3]$   
 $a = a'\sqrt{3} = 2c'$ ,  $c = 4a'$ ,  $V = 16V'$ ,

where  $\text{T}_2^{[6p]}$  or  $\text{Zn}_2^{[6p]} = \text{Zn}$  and  $\text{Zn}/\text{Al}$  or  $\text{Zn}$  only in trigonal prismatic coordination;  $\text{T}$  or  $\text{Zn} = \text{Zn}$  and  $\text{Zn}/\text{Al}$  or  $\text{Zn}$  only in kagomé nets;  $(\text{Zn}/\text{Al}-\text{Zn}/\text{Al}) =$  dumbbells.

The numbers before the square brackets represent the fraction of both segments. Therefore, the content of the unit cell can be obtained by multiplying the formulas by 6, 9, 18 and 16, respectively.

Two kinds of disorders are found in structures (1), (2) and (3). One disorder is due to the partial replacement of ytterbium by pairs of  $\text{Zn}/\text{Al}$  atoms which happens in one of the two independent layers containing ytterbium in structures (1) and (2), whilst the replacement is complete in the other layer. Instead, it is always partial in structure (3) wherever the substitution occurs.

The other kind of disorder is a substitutional disorder due to the mixed  $\text{Zn}/\text{Al}$  occupation of several sites. No order is shown by the aluminium atoms, but they fill all the pairs sharing the sites with zinc. Moreover, in structure (1) with higher Al content (11 at%), a six-fold site at  $z = 0$  is also filled with a  $\text{Zn}/\text{Al}$  mixture. All these positions allow the Al atoms to form the shortest distances with the Yb atoms. The kagomé nets in between remain ordered and formed only by zinc atoms. The behaviour of the Al atoms in these phases is quite different from what is observed in the cited  $\text{Yb}-\text{Fe}-\text{Al}$  system [19], where aluminium actually avoids the dumbbells sites in low Al content phases.

Within the accuracy limits of a refinement from powder data, in structure (4) with the greatest Al content (17 at%) only substitutional disorder is found: all sites are occupied by  $\text{Zn}/\text{Al}$  mixtures with the exception of the  $8c$  position which is filled by zinc.

## 5. Conclusions

The crystal structures of four ternary phases of the  $\text{Yb}-\text{Zn}-\text{Al}$  system have been determined. They are all localized in the zinc-rich corner with compositions in the 71–85 at% Zn range, and are formed by peritectic reaction at temperatures ranging from 715 to 750 °C.

All the examined phases have cells which are multiple of the parent  $\text{CaCu}_5$  type and their atomic arrangements can be obtained by replacing some Yb atoms with  $\text{Zn}/\text{Al}$  dumbbells. The structures of  $\text{Yb}_{3.36}\text{Zn}_{30.94}\text{Al}_{4.34}$ ,  $\text{Yb}_{12.4}\text{Zn}_{96.8}\text{Al}_{4.4}$  and  $\text{Yb}_3\text{Zn}_{17.7}\text{Al}_{4.3}$  are related to the  $\text{SmZn}_{11\sim}$ ,  $\text{U}_2\text{Zn}_{17}$  and  $\text{Ce}_3\text{Zn}_{22}$  types, respectively, whereas  $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$  shows its own structure. No order is found for the Al atoms, but at low Al content, as in  $\text{Yb}_{12.4}\text{Zn}_{96.8}\text{Al}_{4.4}$  (3.9 at% Al) and  $\text{Yb}_{6.4}\text{Zn}_{46.8}\text{Al}_{3.4}$  (6.0 at% Al), they prefer to share the dumbbell sites with zinc. With increasing the Al content, in  $\text{Yb}_{3.36}\text{Zn}_{30.94}\text{Al}_{4.34}$  (11.2 at% Al), besides the dumbbells, another site has also mixed  $\text{Zn}/\text{Al}$  occupation, whilst all sites are occupied by  $\text{Zn}/\text{Al}$  in  $\text{Yb}_3\text{Zn}_{17.7}\text{Al}_{4.3}$  (17.2 at% Al), except for one which is only filled with zinc.

Thermal treatment is a crucial point in obtaining these phases since alloys with the same nominal composition can lead to different compounds depending on the annealing temperature. Further details regarding the formation and thermal stability of the ternary  $\text{Yb}-\text{Zn}-\text{Al}$  compounds, as well as a broader discussion on the crystal chemistry of these phases, will be reported in a future article.

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